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Photoassisted Water-Gas Shift Reaction on Platinized Titania:

The Influence of Preparation Parameters

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(OH(-))

Photoassisted Water-Gas Shift Reaction on Platinized Titania:
The Influence of Preparation Parameters[a]

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Abstract

The variation of the rate of the photoassisted water-gas shift reaction over platinized titania with changes in catalyst preparation has been studied. The following parameters were varied: (1) extent of hydrogen reduction, (2) Pt loading, (3) method of depositing Pt, (4) light intensity and (5) NaOH loading. The reaction rate does not depend on the method of Pt deposition, is first order in light intensity, is not dependent on the chemical state or the Pt loading above 2 wt. %, depends on reduction of the titania and is strongly dependent on the surface concentration of NaOH. From this work, we conclude that when NaOH is present the rate limiting step in the reaction is the reaction of photoproduced holes with surface OH⁻ ions.

1. Introduction

Photoassisted catalytic reactions are of great current interest[1] because of their potential for using solar photons as an energy source for driving reactions that have a significant activation energy and are either exothermic or endothermic. In previous reports from this laboratory we have characterized the activity of platinized titania, Pt/TiO$_2$, for the decomposition of liquid water[2] and for the water-gas shift (WGS) reaction.[3] Coating the catalyst with NaOH improves the performance of Pt/TiO$_2$ for both reactions.[3]

In further efforts to characterize such systems, we investigated several experimental parameters which could influence the rate of the water-gas shift reaction, CO + H$_2$O = CO$_2$ + H$_2$. A summary of the results is presented in this paper. We chose not to study water decomposition directly because of the complications introduced by the fast back reaction on Pt-containing catalysts. In earlier work we have noted that the photoassisted decomposition of water molecules is an important part of the water-gas shift mechanism.[3]

2. Experimental

2.1 Preparation of Catalysts. Sieved TiO$_2$ (MCB, Anatase) with a particle size between 125 and 250 um was reduced for 6 hr in flowing H$_2$ (30 ml/min) at either 700 or 875°C. X-ray powder diffraction, XRD, indicated no measurable rutile in the starting material. After reduction at 700°C, no measureable rutile was detected but after 875°C reduction, a significant amount was found.

Two methods were used to platinize the titania: photodecomposition and impregnation. In the former, both 2 and 10 wt.% Pt/TiO$_2$ samples were prepared from 1.0 g amounts of titania suspended, by bubbling N$_2$, in an acetic acid-sodium bicarbonate buffer solution (pH = 4).[4] The buffered concentration of chloroplatinic acid, H$_2$PtCl$_6$, was 0.005 and 0.05 M for the lower and higher loading, respectively. A 200 W high pressure Hg lamp irradiated the solution for 5.5 and 12 hr., respectively, to achieve the desired Pt loading. The samples were washed with distilled water until no Cl$^-$ ion could be detected in the wash water and then the samples were dried overnight at 120°C.

In the impregnation method, 1.0 g of reduced TiO$_2$ was added to the stoichiometric amount of 0.005 M aqueous H$_2$PtCl$_6$ solution. The mixture was then heated with continuous stirring until it became dry at 120°C and was then heated in air at 350°C overnight.

All of the sodium hydroxide coated catalysts, NaOH/Pt/TiO$_2$ and NaOH/TiO$_2$, were prepared in the reactor by injecting 0.1 M aqueous NaOH solution, 1.2 or 1.8 ml, over 0.2 g of catalyst, previously ground in an agate mortar, and then drying at 40°C in flowing He. This material was then outgassed under vacuum for 3 hours at 200°C as described in section 2.2.

2.2 Apparatus and Procedures. The apparatus has been described previously.[2] The catalyst (0.2 g) was ground in an agate mortar and spread uniformly over the flat bottom (16 cm^2) of the reactor (volume = 200 ml). The catalyst prepared by impregnation was activated with 300 Torr H$_2$ at 200°C for one hour, while for photodeposited catalyst, this step was omitted. The catalysts were all outgassed under vacuum for 3 hr at 200°C.

In most experiments, water vapor (20 Torr) was introduced into the system prior to the introduction of CO (0.5 to 0.7 Torr). Both reactants were circulated through the reaction loop for at least 10 min prior to irradiation. After setting the reaction temperature at 27°C with a water bath, the reaction was initiated by illuminating the catalyst with a 200W Hg lamp. The gas phase was sampled at various times and analyzed with a mass

spectrometer (CEC 21-614) after passing through a cold trap at -110°C to remove water. Between experiments the reaction vessel was demounted and cleaned ultrasonically using alumina powder suspended in water.

X-ray powder diffraction patterns were taken on a General Electric XRD-5 diffractometer with a scan rate of 1°/min. Light intensities were calibrated using an Eppley thermopile and were varied by putting calibrated screens between the light source and the reaction vessel.

3. Results

3.1 H_2 Doping. The bulk conductivity of titania is increased by partial reduction in H_2 at elevated temperatures. The extent of reduction (doping) is controlled by the time and temperature of the process. Catalysts prepared by impregnation were used in this comparison and all of them are listed in Table 1 (catalysts 1,2,3,4,5 and 7). Catalysts 1,2 and 5 were prepared from 3,4 and 7, respectively.

The water-gas shift, WGS, reaction was followed by measuring the H_2 partial pressure as a function of time. Previous work has shown the excellent stoichiometric relation that is realized for H_2 and CO_2 in this system.(3) The reaction is very nearly zero order in CO partial pressure between 0.3 and 0.75 Torr.(3) so the CO partial pressures (0.5 to 0.7 Torr) used in this study will not cause measurable variations in the reaction rate.

The results of six experiments are summarized in Fig. 1. With the exception of catalyst 5 which shows a slight early decay of the rate, all the catalysts show constant rates of H_2 production over the time intervals investigated. Comparing 2 and 4, we see that adding NaOH to an undoped catalyst increases the activity by about two/ orders of magnitude. Comparing 1 with 3 and 5 with 7, indicates a somewhat/ smaller effect (a factor of 20 to 50) of NaOH for the doped catalysts. Doping temperatures between 700 and 875°C do not alter the rate significantly but an undoped sample, i.e. only exposed to H_2 at 200°C as described in the experimental section, is a poorer catalyst by about an order of magnitude. Care must be exercised here in that small variations from preparation to preparation are significant. However, all of our results suggest that undoped catalysts are significantly lower activity than their doped counterparts. For example, compare 1 with

effect and gives results like those of sample 12 (i.e. the background rates were always at least a factor of 20 lower than the rates measured with active catalysts). The residual activity observed with sample 11 is very interesting. If the Pt is located on the reaction vessel walls, then photoassisted activity involves Pt/SiO_2 but the band gap of the latter (8-11 eV) is too large to make use of most of the radiation from the lamp. Perhaps the residual Pt is removed from the walls during the catalyst preparation and becomes physically attached to the titania. In either case the decay of the initial rate with time sets catalyst 11 apart from the others of Fig. 3.

3.4 NaOH Loading. Samples 10, 13 and 14 of Table 1 came from the same batch of Pt/TiO_2 and the NaOH loading was varied from 0 to 5.3 wt.%. Significant increases in H_2 production rates were found varying from 0.5 to 8 to 19 μmole/hr/(g of Pt/TiO_2) with increasing NaOH. These results clearly show that additions of NaOH are much more effective for rate increases than extensive reduction in H_2.

3.5 Light Intensity. Sample 13 was used in evaluating the role of light intensity on the rate of hydrogen production. The dark reaction rate was 0.6 μmole/hr/g while under illumination of the full arc (100%) the rate was 19 μmole/hr/g. For relative intensities of 52 and 22% the rates were 10 and 5 μmole/hr/g respectively. Over the 50 min period studied at each intensity, the rate showed only very slight tendency to drop. Correcting each of the photoassisted rates for the background gives the curve shown in Fig. 4 showing a linear relation with relative light intensity. The flux incident on the sample at 100% relative intensity corresponds to 0.21 watt/cm^2.

in Fig. 1 and Table 1. Since a significant amount of bulk rutile is formed during reduction at 875°C, whereas anatase dominates after reduction at 700°C, we conclude that the bulk anatase-to-rutile ratio does not influence the rate significantly.

3.2 Pt Deposition Method. The Pt deposition method has no detectable influence on the rate of the WGS reaction in these experiments. Comparing the photodeposition method with the impregnation method with (samples 5 and 6) and without (samples 7 and 8) NaOH shows that H_2 production rates are independent of the deposition method. Further characterization of these samples was done using XRD, Fig. 2. A broad Pt peak was observed in both samples consistent with an average particle size of about 80 Å diameter for both cases based on H_2 chemisorption. These results are consistent with STEM results(8) showing an average particle diameter of 100Å.

3.3 Platinum Loading. Using a set of four catalysts from the same batch of doped TiO_2 (700°C in H_2 for 6 hr), the Pt loading was varied from 0 to 10 wt.%. The results are summarized in Fig. 3 and Table 1 (samples 9-12).

Comparing samples 10 and 6 which were taken from two different batches of reduced TiO_2, we conclude that the reproducibility is about $\pm$ 10%. While the reproducibility within a given batch is significantly better, caution must be exercised in interpreting small differences. For example, comparing samples 9 and 10 suggests a small rate enhancement in passing from 2 to 10 wt.% Pt but this is not conclusive. In any event, we can conclude that such increases in the Pt loading are of little value. Sample 11 is an interesting case. It was run after experiment 10 was completed and the reaction cell was cleaned ultrasonically with water as the solvent. We attribute the initial rate of 8 μmole/g hr to a small amount of residual Pt left on the walls of the reaction vessel. Cleaning the reaction vessel ultrasonically with alumina powder suspended in water always eliminates this

4. Discussion

The increased rate of the WGS reaction upon reducing (doping) the titania is attributed primarily to the increased rate at which holes move to the surface. Hydrogen treatment removes lattice oxygen atoms leaving defects and Ti^{3+} ions. This process makes titania more n-type and increases the conductivity of pellets of the powder.[8] This is equivalent to noting that the Fermi level of the titania is raised toward the vacuum level and, with heavy doping, comes close to the bottom of the conduction band. From this point of view, there is greater band bending at the electrolyte-titania interface and at the Pt/TiO_2 interface upon doping. In the language of Wolkenstein[5], the relative hole concentration at the surface, or its reaction product, is given by:

$$\eta^+ = \frac{\exp\{2V_s/kT\}}{1 + \cosh\{2V_s/kT\}}$$

where η^+ is the fraction of the "positively charged form" of chemisorption on the surface in the presence of illumination and V_s denotes the band bending. According to this equation the band bending supplies the potential energy for separating the optically generated hole-electron pairs. The larger V_s, the faster the majority current carriers (electrons) move to the bulk and the less competitive hole-electron recombination becomes. Consequently the fraction of holes and their absolute concentration both increase with band bending.

Absorption spectrum changes associated with reduction in H_2, for example, a broad new band around 1500 nm[6] cannot be responsible for the changes in activity because a 415 nm cut-off filter completely retarded the WGS reaction.[3] From this we conclude that photons with energies less than the bandgap of titania are not active in assisting the WGS reaction.

Recently, strong metal-support interactions (SMSI) have received considerable attention with respect to both underlying principles and possible applications. For example, it has been shown that Pd supported on TiO_2 in the SMSI state, i.e. titania reduced at elevated temperatures, is much more active in CO hydrogenation than either alumina- or silica-supported Pd.[7] This enhancement is attributed to increased relative coverage of hydrogen. The SMSI state only weakly chemisorbs both hydrogen and carbon monoxide but the effect on CO coverage is more pronounced than hydrogen. However, in the photoassisted WGS reaction, the SMSI effect has no pronounced influence on the rate. Catalyst 1 which shows SMSI character and catalyst 5 which does not[8] both have the same activity for the WGS reaction. The SMSI state is here defined as a condition where the catalyst will not chemisorb measurable amounts of hydrogen at room temperature and at pressures up to 400 Torr. This suggests that mechanistic steps involving the nature of Pt/TiO_2 interactions are not rate controlling under our conditions. For example, the desorption of H_2 and the transfer of electrons from the conduction band of TiO_2 to the Pt are not rate controlling. It is important to note here that our preparation method involves reduction of the titania prior to adding the Pt. Some oxidation of the surface region occurs upon exposure to air and the platinization process and this may account for the fact that we find no SMSI effect without reduction at temperatures greater than $700^\circ C$ whereas others have found in-situ reduction at $500^\circ C$ to be sufficient.[10]

The influence of Pt loading beyond 2% is minor, indicating that the rate is not controlled by the amount of Pt at the surface in this range. However, some Pt is beneficial as indicated by catalysts 11 and 12. The rapid initial rate, followed by a rather rapid decline, observed for catalyst 11 remains puzzling. Further work is necessary to understand this
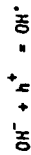
determining step of the mechanism previously proposed:[3]

$$OH^- + h^+ = OH\cdot$$

which is also probably the rate determining step in the photoassisted liquid water decomposition reaction over NaOH/Pt/TiO$_2$ catalysts.[3] This kind of rate-controlling process is shown schematically in Fig. 5.

behavior but we speculate that it is related to the local OH$^-$ concentration and the nature of the residual Pt/TiO$_2$ interaction. It appears that 2 wt.% Pt loading provides enough active sites for electron collection and reaction with water molecules to make H$_2$ and also stabilizes the catalyst activity. Similar results and conclusions about Pt loading are drawn by Borgarello, et al.[9] from their results on water cleavage in colloidal TiO$_2$ systems. They observed on colloidal particles that loading greater than 2 wt.% Pt gave little increase in hydrogen yield.

Since neither loadings greater than 2 wt.% Pt nor the presence/absence of SMSI Pt has a significant influence on the rate, it is not surprising that catalysts prepared by the photodeposition and impregnation methods have almost the same activity. The latter is preferred operationally just because the former is much more time consuming and more complicated.[4]

As noted earlier, adding NaOH gives the greatest improvement in the rate, the 3.5 wt.% NaOH (sample 10) having 16 times the rate of the corresponding 0 wt.% material (sample 14). Earlier work from this laboratory gave a factor of 2.5 rate increase for a 4 wt.% NaOH loading. We attribute this difference to larger surface areas intercepting radiation in the present experiments since the materials used here were ground in an agate mortar after platinization but before adding NaOH. Significant enhancement by OH$^-$ of the photoassisted water decomposition reaction on SrTiO$_3$ system has also been reported by Wagner et al[11].

The light intensity study shows that for our conditions there is no evidence for rate control involving reactions between more than one photogenerated species. Since the rate is first order in the light intensity, we do expect that one photo-derived species will participate. Moreover the quantum efficiency is no more than a few percent so the process is non-catalytic in photons. Since electrons are the majority carriers in our n-type titania and since the reaction requires band gap radiation, we propose that holes, the minority carriers, are involved in the rate

5. Conclusions.

The present study establishes several important features concerning the performance of NaOH/Pt/TiO$_2$ substrates in the photoassisted water-gas shift reaction and suggests that the process in which hydroxide ion donates its electron to the surface hole is rate determining. Those parameters which increase the surface hole population, like reduction in H$_2$, higher light intensity and higher NaOH loading, suggest that improved hole generation rates, electron-hole separation and hole utilization at the surface are useful routes to improved performance.

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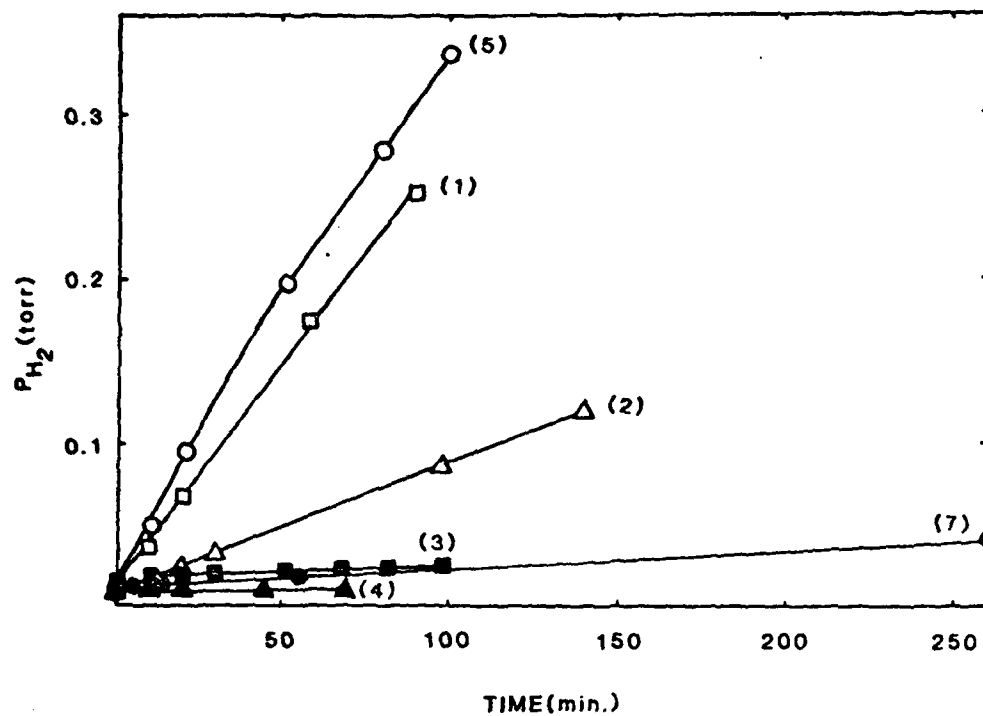| No.	Catalyst	Wt.% Pt	Wt.% NaOH	Prep. Method	Doping Temp/C	H_2 Production[d] μmole/(g hr)
1	NaOH/Pt/TiO$_2$	2	3.5	I[b]	875	9
2	NaOH/Pt/TiO$_2$	2	3.5	I	---	3
3	Pt/TiO$_2$	2	0	I	875	0.2
4	Pt/TiO$_2$	2	0	I	---	0.04
5	NaOH/Pt/TiO$_2$	2	3.5	I	700	9
6	NaOH/Pt/TiO$_2$	2	3.5	P[c]	700	9
7	Pt/TiO$_2$	2	0	I	700	0.4
8	Pt/TiO$_2$	2	0	P	700	0.6
9	NaOH/Pt/TiO$_2$	10	3.5	P	700	9
10	NaOH/Pt/TiO$_2$	2	3.5	P	700	8
11	NaOH/ /TiO$_2$	tr[a]	3.5	-	700	8[e]
12	NaOH/ /TiO$_2$	0	3.5	-	700	0.4
13	NaOH/Pt/TiO$_2$	2	5.3	P	700	19
14	Pt/TiO$_2$	2	0	P	700	0.5

(a) A small amount of residual Pt from the previous experiment remained after cleaning the reactor ultrasonically with water.
(b) Impregnation method.
(c) Photodecomposition method
(d) The flux of photons with energy greater than the band gap (3.1 eV) of anatase is about 10^{17} cm^{-2} sec^{-1}. The rate quoted was measured between 50 and 75 min using data shown in Fig. 1.
(e) Initial rate.

Figure Captions.

Figure 1. H_2 reduction effect on (3.5 wt.%)NaOH/(2 wt.%)Pt/TiO$_2$,open symbols, and (2 wt.%)Pt/TiO$_2$, closed symbols, prepared by impregnation.

O,● – 875°C in H_2 flow for 6 hr.

□,■ 700°C in H_2 flow for 6 hr.

Δ,▲ without H_2 pretreatment.

Figure 2. X-ray powder diffraction patterns for Pt/TiO$_2$ catalysts prepared by impregnation (sample 7) and photodecomposition (sample 8).

Figure 3. Effect of Pt loading on (3.5 wt.%)NaOH/(700°C reduced)TiO$_2$. O-10 wt.%, Δ-2 wt.%, □-trace of Pt, ●-Pt-free.

Figure 4. Variation of H_2 production rate with relative light intensity, corrected for small background rate.

K = (Rate with light - Rate in dark)/(Rate in dark)

Figure 5. Schematic description of proposed rate-controlling step in the water gas shift reaction.

Fang et al. Fig.1

Fang et al. Fig.2

Fang et al. Fig. 3

Relative Light Intensity

Fang et al, Fig. 4.

HO^- $h\nu$ rds $\left[HO^- \oplus \rightarrow \ominus \right]$ very fast HO

TiO_2 TiO_2 to bulk of semiconductor TiO_2
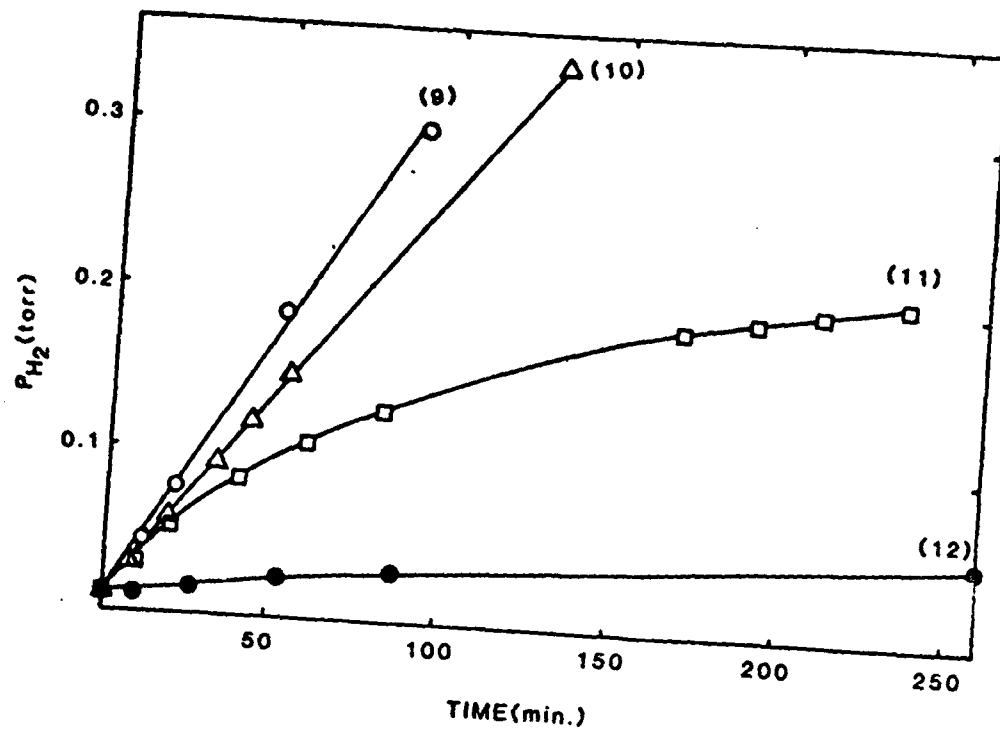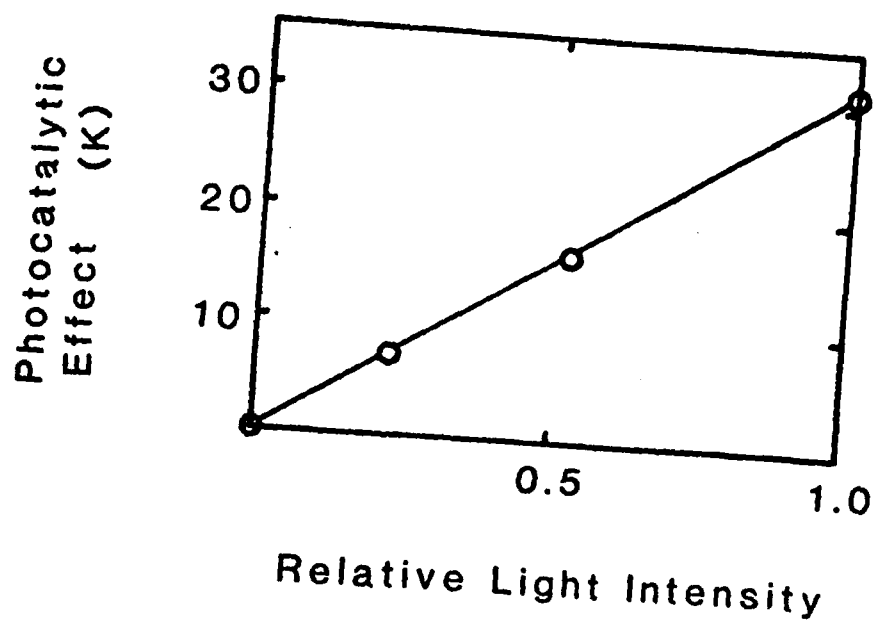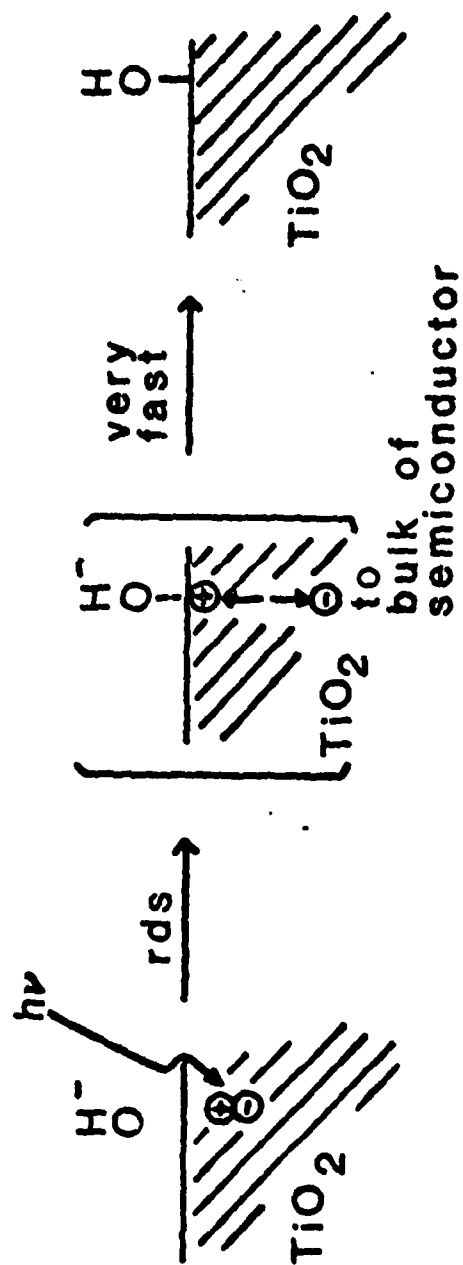
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